

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B32B 27/34, B65D 65/40	A1	(11) International Publication Number: WO 99/12735 (43) International Publication Date: 18 March 1999 (18.03.99)
(21) International Application Number: PCT/US98/18731 (22) International Filing Date: 8 September 1998 (08.09.98) (30) Priority Data: 97202750.2 8 September 1997 (08.09.97) EP (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): TROUILHET, Yves [FR/CH]; 4, chemin des Tattes, CH-1222 Vésenaz (CH). (74) Agent: EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PACKAGING MATERIAL (57) Abstract A flexible or semi-flexible packaging material with an oxygen barrier between 10 and 100 cc/m ² d atm and a water vapor barrier between 100 and 1000 g/m ² d at 38 °C and 90 % relative humidity is disclosed. It contains (a) a layer of paper having a weight between 20 and 400 g/m ² , (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight between 1 and 5 g/m ² adjacent to layer (a), and (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10 and 30 g/m ² adjacent to layer (b). This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE

PACKAGING MATERIAL

5

The present invention relates to packaging for food products that are sensitive to oxidation, including dairy products such as cheese, butter and margarine.

Background of the invention

10

Various materials for providing oxygen barriers for products sensitive to oxidation are known, including ethylene vinyl alcohol (EVOH), amorphous nylon, semicrystalline polyamide 6 and polyacrylonitrile.

15

For packaging liquid or semi-liquid materials that are sensitive to oxidation, water barrier properties are also needed. C.f. EP 0241 819, which discloses a laminate using nylon as a barrier; EP 0293 098, which discloses a multilayer structure with EVOH and low density polyethylene (LDPE) coated on board. More recently, EP 0520 767 discloses the use of amorphous nylon as a non-foil composite laminate. In all of these cases, water vapor transmission is below 10 g/m²d due to a relatively thick polyethylene seal layer.

20

In soft cheese packaging the right balance of an oxygen barrier and a moisture barrier is given by a cellulosic film laminate to paper. In this case, the water vapor transmission is between 400 and 630 g/m²d at 38 °C and 90% relative humidity (RH), while the oxygen permeability is below 10 cc/m²d atm.

25

Summary of the invention

30

The present invention provides a flexible or semi-flexible packaging material with an oxygen barrier between 10 and 100 cc/m²d atm and a water vapor barrier between 100 and 1000 g/m²d at 38°C and 90% relative humidity comprising (a) a layer of paper having a weight between 20 and 400 g/m², (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight between 1 and 5 g/m² adjacent to layer (a), and (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10 and 30 g/m² adjacent to layer (b). This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine.

35

40

The packaging material may be made by means known in the art such as by coextrusion coating or lamination of coextruded film onto paper.

Detailed description of the invention

45

As used herein, the following terms have the meanings given below.

'Flexible packaging material' means packaging sheet material suitable for wrapping goods, e.g. the aforementioned dairy products. 'Semi-flexible packaging material'

means packaging material having a somewhat higher resistance to flex, typically having a board (e.g. cardboard) as paper layer (a). Semi-flexible packaging material may be thermoformed, as known in the art, to form desired shapes, such as trays.

- 5 'Oxygen barrier' measures the rate at which oxygen passes through the packaging material of the present invention, and is between 10 and 100 cc/m²d atm measured according to ASTM D 3985.

- 10 'Water vapor barrier' measures the rate at which water vapor passes through the packaging material of the present invention, and is between 100 and 1000 g/m²d at 38°C and 90% relative humidity.

- 15 Paper layer (a) can be any type of paper typically used in the packaging industry, flexible or semi-flexible, and having a weight between 20 and 400 g/m². This weight governs the degree of flexibility of the paper. Paper, being a very porous material, does not control the oxygen or water vapor barrier properties of the packaging material of the present invention.

- 20 The ethylene copolymer of layer (b) can be ethylene vinyl acetate, ethylene-ethyl acrylate, ethylene-methyl acrylate or ethylene butyl acrylate, an ethylene-acid copolymer or its corresponding ionomer.

- 25 The ethylene-acid copolymers are copolymers of ethylene and α,β -ethylenically-unsaturated C₃-C₈ carboxylic acid have the acid moiety present in an amount of 1 to about 25, (preferably 6 to 9) wt. % of the copolymer. The preferred acid moieties are methacrylic acid and acrylic acid.

- 30 The ethylene-acid copolymers can also be E/X/Y copolymers where E is ethylene; X is a softening comonomer and Y is the α,β -ethylenically-unsaturated C₃-C₈ carboxylic acid, particularly acrylic or methacrylic acid. By "softening", it is meant that the polymer is made less crystalline. Suitable "softening comonomers (X) are monomers selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1 - 12 carbon atoms which, when present, may be up to 25 (preferably up to 15, most preferably up to 10) wt. % of the ethylene-acid copolymer.

- 35 Specific ethylene-acid copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate.

- 45 Corresponding ionomers of the ethylene-acid copolymers are formed by partially neutralizing the acid moiety. The acid moiety is partially neutralized with monovalent and/or bivalent metal cations such as lithium, sodium*, potassium, magnesium, calcium, barium, lead, tin, zinc* or aluminum (*= preferred), or a combination of such

cations. The mole percent of acid neutralized is up to about 70 %, preferably 30 to 50 %.

5 Ionomers can be made by processes well known in the art (cf. U.S. Pat. No. 3,262,272 to Rees, for example).

The graft of the ethylene copolymer will be maleic anhydride, typically in an amount between 0.1 and 3 weight %. Grafting can be carried out using techniques known in the art.

10 Optionally, layer (b) may further comprise up to 40 weight % of a copolyether ester, a copolyether amide or a polyurethane thermoplastic. Suitable copolyether esters are available under the name Hytrel® from the DuPont Company; suitable copolyether amides are available under the name Pebax® from Elf Atochem.

15 Layer (b) will be applied to paper layer (a) at a weight between 1 and 5 g/m² to assure the desired oxygen and water vapor barrier levels of the present invention are met. Suitable ethylene copolymers for use in layer (b) are the Bynel® and Surlyn® families of resins, both available from the DuPont Company.

20 Nylon layer (c) can contain pure amorphous nylon or can be a blend of between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6.

25 The term "amorphous polyamide" is well known to those skilled in the art. "Amorphous polyamide", as used herein, refers to those polyamides which are lacking in crystallinity as shown by the lack of an endotherm crystalline melting peak in a Differential Scanning Calorimeter ("DSC") measurement (ASTM D-3417), 10 °C/minute.

30 Examples of the amorphous polyamides that can be used include those amorphous polymers prepared from the following diamines: Hexamethylenediamine, 2-methylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, bis-(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)isopropylidene, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, meta-xylylenediamine, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethyldiaminobutane, 1,4-diaminomethylcyclohexane, p-xylylenediamine, m-phenylenediamine, p-phenylenediamine, and alkyl substituted m-phenylenediamine and p-phenylenediamine.

40 Examples of polyamides that can be used include those amorphous polymers prepared from the following diacidic acids: isophthalic acid, terephthalic acid, alkyl substituted iso- and terephthalic acid, adipic acid, sebacic acid, butane dicarboxylic acid, and the like.

45 Specific examples of amorphous polyamides which are suitable for this invention include: hexamethylenediamine isophthalamide, hexamethylenediamine isophthalamide/terephthalamide, copolymers of hexamethylene diamine and 2-

methylopentamethylenediamine with iso-or terephthalic acids, or mixtures of these acids. Polyamides based on hexamethylenediamine iso/terephthalamide containing high levels of terephthalic acid moiety may also be useful provided a second diamine such as 2-methyldiaminopentane is incorporated to produce a processible amorphous polymer.

The above amorphous polyamides may contain as comonomers minor amounts of lactam species such as caprolactam or lauryl lactam, even though polymers based on these monomers alone are not amorphous. The important feature is that the polyamide as a whole must be amorphous. Thus small amounts of these comonomers may be incorporated as long as they do not impart crystallinity to the polyamide. In addition, up to about 10 weight % of a liquid or solid plasticizer such as glycerol, sorbital, mannitol, or aromatic sulfonamide compounds (such as Santicizer 8® from Monsanto) may be included with the amorphous polyamide.

A suitable amorphous polyamide for use in the present invention is available from the DuPont Company under the tradename SELAR®PA.

The term "semicrystalline polyamide 6" is well known to those skilled in the art. Semicrystalline polyamide 6 suitable for this invention are generally prepared from lactams or amino acids or from condensation of diamines such as hexamethylene diamine with dibasic acids such as sebacic acid. Copolymers and terpolymers of these polyamides are also included. A suitable semicrystalline polyamide 6 for use in the present invention is Durethan® B29, available from Bayer.

Layer (c) will be applied to paper layer (b) at a weight between 10 and 30 g/m² to assure the desired oxygen and water vapor barrier levels of the present invention are met.

This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine. It will be typically be produced by coextrusion coating of layers (b) and (c) onto layer (a), or by lamination of extruded or coextruded layers (b) and (c) onto layer (a). Optionally, the so prepared packaging material can be subsequently thermoformed into a desired shape, such as a tray.

Example 1

Layer (b) of Bynel® 21E533 (an anhydride modified ethylene acrylate resin from DuPont) is coextruded with layer (c) of various blend of Selar® PA 3426 (an amorphous nylon from DuPont) and Durethan® B29 (a semicrystalline polyamide 6 from Bayer) and coated on paper.

The nylon blend is introduced into a 3.5" extruder with barrel temperatures set at 240, 280, 280, 280 and 280 °C. The Bynel® 21E533 is introduced in 2.5" extruder with barrel temperatures set at 180, 220, 250, 270, 280 °C. Feed bloc and die temperatures are set at 280°C.

The 800 mm wide die is 150 mm (air gap) above the nip where it coats the paper. The paper is corona treated and run at the line speed of 200 m/min. The final so produced structure is:

5 paper // The Bynel® 21E533 // Selar® PA3426+Durethan® B29
 40 g/m² 2 g/m² 12 g/m²

The following water transmission (38°C, 90% RH) and oxygen permeability (room temperature) is measured (% given by weight):

10	Example				water	oxygen
					g/ m ² d	cc/ m ² d atm
	1.1	80% Selar® PA3426 + 20% Durethan® B29			400	32
15	1.2	50%	"	+ 50%	500	35
	1.3	20%	"	+ 80%	800	43

The last two structures are particularly well suited for soft cheese packaging.

20 Example 2

Example 1 is repeated except that Surlyn® AD2 is substituted for Bynel® 21E533.

25 Surlyn® AD2 (2 g/m²) is coextruded with the blend 80 weight % Selar® PA3426 + 20 weight % Durethan® B29 (12 g/m²). The oxygen permeability is the same as in Example 1.1. Water permeability lowers to 250 g/m²d.

This structure when extruded on a glossy chill-roll has a very glossy appearance. Together with the dead-foil, it can be used for candy and butter wrapping.

30

Example 3

35 Example 2 is repeated except that the paper layer is replaced with board having a weight of 200 g/m². The board can be thermoformed to produce trays or lidding.

Example 4

40 Example 1 is repeated except that the 70 wt. % Bynel® 21E533 and 30 wt % Hytrel® 3548 is substituted for Bynel® 21E533.

Claims

1. A flexible or semi-flexible packaging material with an oxygen barrier between
5 10 and 100 cc/m²d atm and a water vapor barrier between 100 and 1000 g/m²d at
38°C and 90% relative humidity comprising
- (a) a layer of paper having a weight between 20 and 400 g/m²
- 10 (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight
between 1 and 5 g/m² adjacent to layer (a), and
- (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon
and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10
15 and 30 g/m² adjacent to layer (b).
2. The packaging material of claim 1 wherein the ethylene copolymer of layer (b)
is ethylene vinyl acetate, ethylene-ethyl acrylate, ethylene-methyl acrylate or
ethylene butyl acrylate.
- 20 3. The packaging material of claim 1 wherein the ethylene copolymer of layer (b)
is an ethylene-acid copolymer or its corresponding ionomer.
4. The packaging material of claim 1 wherein the grafted ethylene copolymer of
25 layer (b) is a maleic anhydride grafted ethylene copolymer.
5. The packaging material of any one of claims 1 to 4 wherein layer (b) further
comprises up to 40 weight % of a copolyether ester, a copolyether amide or a
polyurethane thermoplastic.
- 30 6. The packaging material of any one of claims 1 to 5 which is produced by
coextrusion coating layers (b) and (c) onto layer (a).
7. The packaging material of any one of claims 1 to 5 which is produced by
35 lamination of extruded or coextruded layers (b) and (c) onto layer (a).

INTERNATIONAL SEARCH REPORT

Application No
PCT/US 98/18731

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/34 B65D65/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 551 366 A (MARUHASHI YOSHITSUGU ET AL) 5 November 1985 see column 2, line 26-41 - column 4, line 49-65-66; claims 1,3,4,7,8,17; figures 1,3,4,7,8	1,4,6
Y	see column 5, line 3-19-25 - column 7, line 65-68 see column 8, line 5-19-25 - line 39-43 see column 9, line 64-67 - column 10, line 4-20-57	1-3
Y	DE 40 26 040 A (PKL VERPACKUNGSSYSTEME GMBH) 8 August 1991 see column 1, line 49; claims 1,2 --- -/--	1-4,6,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

17 December 1998

Date of mailing of the international search report

30/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Derz, T

INTERNATIONAL SEARCH REPORT

Int. No. Application No.
PCT/US 98/18731

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 687 557 A (ENSO GUTZEIT OY) 20 December 1995 see column 3, line 12-43; claims 4,9,10; figures 3,4	1,4,6,7
A	EP 0 520 767 A (WESTVACO CORP) 30 December 1992 cited in the application see claims 1,4,5; figure 3A	1,4,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Application No

PCT/US 98/18731

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4551366	A	05-11-1985	JP 1384118 C	09-06-1987
			JP 58154755 A	14-09-1983
			JP 61049341 B	29-10-1986
			AU 557675 B	08-01-1987
			AU 1001583 A	18-08-1983
			EP 0084421 A	27-07-1983
			ZA 8300079 A	29-02-1984
DE 4026040	A	08-08-1991	EP 0441234 A	14-08-1991
EP 0687557	A	20-12-1995	FI 942877 A	17-12-1995
			AU 695041 B	06-08-1998
			AU 2171395 A	04-01-1996
			JP 8002555 A	09-01-1996
			US 5840385 A	24-11-1998
EP 0520767	A	30-12-1992	CA 2070349 A	27-12-1992
			JP 2537000 B	25-09-1996
			JP 5229070 A	07-09-1993
			MX 9202891 A	01-12-1992

